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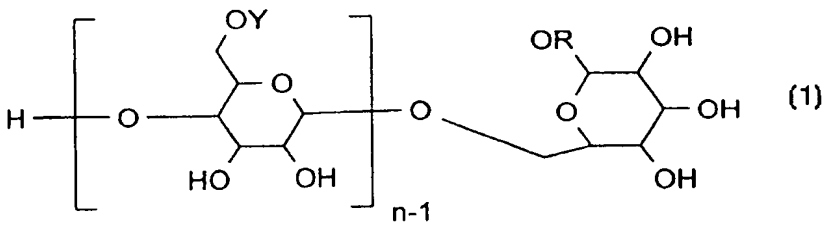

(1)

(57) Abstract

Alkyl polyglycosides of general formula (1) are used as non–crystal–growth–promoting pesticidal adjuvants in aqueous particulate suspension pesticide formulations. The pesticide may be any pesticide which can be formulated as a particulate suspension, but is preferably a pesticide having a solubility in water of not more than 600 ppm. The invention is also particularly applicable to pesticides having a melting point of at least 55 °C.

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PESTICIDAL ADJUVANTS

This invention relates to particulate suspensions of pesticides in water.

It is well known to apply pesticides to crops in the form of an emulsion. However, in the preparation of pesticide emulsions, it is generally necessary to employ an organic solvent (for example, xylene). Fears about the damage that such solvents can cause to the environment have prompted the search for other ways of formulating pesticides, which avoid or reduce the use of solvents. Additionally, some pesticides have only limited solubility in the solvents which are generally employed, so have to be formulated in another way.

One way in which the use of organic solvents can be reduced, is by formulating pesticides as particulate suspensions, for example in an aqueous phase. However, in many cases, the biological efficacy of particulate suspensions of pesticidal actives is very low. It is conventional in order to raise the biological efficacy of such particulate suspensions to employ an adjuvant, which is thought to increase the biological availability of the pesticide. Typical adjuvants used for such purposes are surface active materials, such as alcohol ethoxylates, amine ethoxylates, ethylene oxide/propylene oxide block copolymers, alcohol sulphates, alkylaryl sulphonates, alkylsulphonates, alkylphenol ethoxylates, ester ethoxylates, castor oil ethoxylates or alkanolamides.

Although the use of adjuvants is very effective in increasing the biological efficacy of pesticidal actives, their use in pesticidal formulations which are "one-pack" particulate suspensions generally gives rise to crystal growth (e.g., by means of Ostwald ripening). Crystal growth can occur over the relatively short period of time for which a particulate suspension is stored before use.

Crystal growth by Ostwald ripening generally occurs when smaller crystals (which have a greater total area than larger crystals) dissolve in the continuous phase, and the active material is transported through the continuous phase, to nucleation sites (such as the larger crystals). In addition, aggregation effects can compound sedimentation in and non-homogeneity of the formulation, i.e., the crystals can "clump" together.

Stability problems can also occur in a particulate suspension of a pesticide which does not require an adjuvant, if the formulation also comprises a second pesticide, and an adjuvant is added in order to increase the biological efficacy of the second pesticide. The second pesticide may be dissolved in an aqueous phase and/or dispersed in a non-aqueous phase, or present as a particulate suspension itself.

The inherent instability to storage of particulate suspensions of pesticides formulated with adjuvants has meant that such particulate suspensions have to be used very soon after formulation, which is commercially unsatisfactory. Alternatively, the product and an adjuvant have to be provided separately in a twin-pack, or the use of commercial adjuvant in addition to the product has to be recommended, in order that the adjuvant can be mixed into the particulate suspension or spray tank shortly before it is used. However, it would be more convenient if a storage-stable one-pack formulation of adjuvant and product could be provided.

It has now been discovered that when alkyl polyglycosides are employed as adjuvants for pesticidal compositions which are particulate suspensions, surprisingly their use does not cause significant crystal growth.

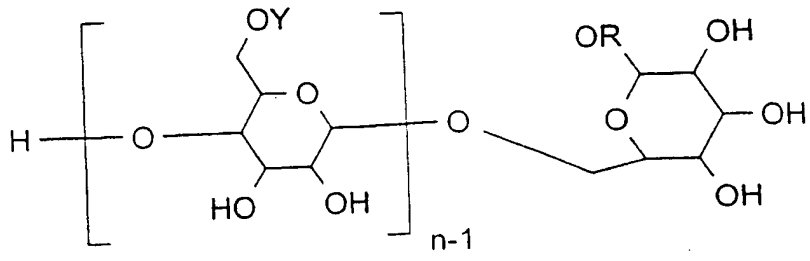
By "alkylpolyglycoside" is meant a chain of one or more saccharide units linked by glycoside bonds which terminates in an alkyl group joined to the terminal saccharide unit by a glycoside bond.

WO-A-9803065 (Dow AgroSciences) discloses a process for preparing a storage-stable aqueous dispersion of microcapsules comprising a supersaturated solution or a supercooled melt of a water-insoluble material (such as a pesticide). The dispersion is stabilised with a non-micellising surfactant, that is a surfactant which does not form micelles under the conditions used to store the stabilised dispersion. There is no suggestion in the reference of the use of alkyl polyglycoside adjuvants.

It has previously been known to use alkyl polyglycosides as adjuvants in the agricultural industry. For example, Henkel supplies alkyl polyglycoside adjuvants under the trade name Agrimul™, and Unquema supplies alkyl polyglycoside adjuvants under the trade name Atplus™.

A number of references disclose the use of alkyl polyglycosides as adjuvants (or dispersing agents) for pesticides, for example US 4888325 (Henkel KgaA) and US Statutory Invention Regulation H224 (Malik *et al.*). DE-A-4229442 (Henkel KgaA) discloses the use of alkyl polyglycosides as biodegradable dispersants in the preparation of dye and pigment compositions. WO 93/22917 (Henkel Corp.) describes the addition of fatty alcohols to alkyl polyglycosides in order to improve wetting ability and the use of aliphatic monoglucosides as adjuvants. WO 98/09518 (Henkel Corp.) relates to the use of additives to improve the tactile and aesthetic properties of alkyl polyglycosides and to prevent their crystallising. However, it has not previously been realised that, alkyl polyglycosides can be employed as adjuvants without causing significant crystal growth of the product formulation.

In accordance with the invention, there is provided the use of an alkyl polyglycoside of general formula [1]



[1]

in a formulation comprising an aqueous particulate suspension of at least one pesticide, as a non-crystal-growth-promoting pesticidal adjuvant,

wherein

R is a C_4-C_{20} alkyl group

n is from 1 to 10,

and Y is H, C_1-C_{20} alkyl, or a group of the formula $(C_qH_{2q}O)_z X$, $-SO_3M$, $-PO_3X_2$, $-COCH_2CH[SO_3M]COOX$, $-COX$, $-(CH_2)_pCOOX$, $-CH_2CH_2SO_3M$, $-COOX$, a quaternary ammonium derivative, or a glycerol residue,

wherein z is from 1 to 50

p is from 1 to 20

q is from 2 to 4

M is H or a suitable counter-ion,

and each X independently is H or C_1-C_{20} alkyl.

R is preferably a C_8-C_{18} alkyl group, and n is preferably from 1 to 3. M may be, for example, H or an ammonium, substituted ammonium (e.g., ammonium substituted with from 1 to 4 C_1-C_6 alkyl groups) ammonium, sodium, potassium, or magnesium ion. Preferably, Y in formula 1 is H.

The term "pesticide" as used herein means any substance which destroys or protects against pests, (i.e, harmful organisms, particularly organisms which are harmful to crops or plants). The term "pesticide" therefore encompasses insecticides, herbicides, fungicides and acaricides.

The pesticide may be any pesticide which can be formulated as a particulate suspension. The invention is particularly applicable to pesticides having a solubility in water of not more than 600ppm, more particularly not more than 150ppm, and most particularly not more than 50ppm. The invention is also particularly applicable to pesticides having a melting point of at least 55°C, more particularly at least 77°C, and most particularly at least 100°C.

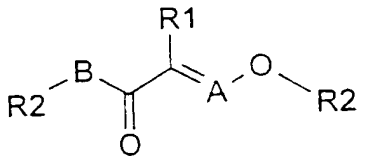
Suitable fungicidal, herbicidal and insecticidal materials having a melting point of at least 55°C and a solubility in water of not more than 600ppm are listed below. In the tables, the names and identifiers are taken from the Pesticide Manual, 11th edition.

Suitable fungicidal materials having a melting point of at least 55°C
and a solubility in water of not more than 600ppm include the following:

	Fungicides	
amitrole (<ph4.2)	azaconazole (<ph3)	azoxystrobin
benalaxyl	benomyl	bitertanol
bromocunazole	captafol	captan
carbendazim	carboxin	chinomethionate
chlorothalonil	chlozolinate	copper oxychloride
cuprous oxide	cyproconazole	cyprodinil
dichlofluanid	dichlorophen	diclomezine
dicloran	diethofencarb	difenoconazole
dimethomorph	diniconazole	dinobuton
dithianon	dodemorph	epoxiconazole
ethirimol	famoxadone	fenarimol
fenbuconazole	fenfuram	fenpiclonil
fentin	ferbam	ferimzone
fluazinam	fludioxonil	fluoroimide
fluquinconazole	flusulfamide	flutolanil
flutriafol	folpet	fuberidazole
furalaxyl	hexachlorobenzene	hexaconazole
imibenconazole	ipconazole	iprodione
kresoxim-methyl	ktu 3616	mancozeb
maneb	Mepanipyrim	mepronil
mercuric oxide	Mercurous chloride	metconazole
methasulfocarb	Metiram	myclobutanil
nickel bis(dimethyldithiocarbamate)	Nitrothal-isopropyl	nuarimol
ofurace	oxine-copper	penconazole

	Fungicides	
pencycuron	Pentachlorophenol	phthalide
probenazole	Promcymidone	propineb
pyributicarb	Pyrimethanil	quinoxyfen
quintozene	ssf-126	sulphur
tebuconazole	Tecnazene	thiabendazole
thifluzamide	Thiophanate-methyl	thiram
tolclofos-methyl	Tolylfluanid	triadimefon
triadimenol	Triazoxide	triforine
triticonazole	Vinclozolin	zineb
ziram		

and strobilurin analogues i.e., a compound of the formula [2]



[2]

wherein R1 is an aromatic or heteraromatic group, preferably a phenyl or substituted phenyl (in particular phenyl substituted with 2-methylphenoxymethylene or 6-(2-cyanophenoxy) pyrimidin-4-yloxy),

R2 is H, or C_1-C_{10} alkyl

A is CH or N and

B is O or NH.

Particularly suitable strobilurin analogues include (2[2-(3-trifluoromethyl)-5-chloro-2-pyridyloxymethyl)phenyl]-2-methoxyimino-N-methylacetamide, kresoxim methyl, and azoxystrobin.

Suitable insecticidal (or acaricidal) materials having a melting point of at least 55°C and a solubility in water of not more than 600ppm include the following:-

Insectides/acaricides		
abamectin	acrinathrin (i/a)	amitraz
	azinphos-methyl	azocyclotin
bensultap	benzoximate (a)	bifenthrin (i/a)
bromopropylate	buprofezin	carbaryl
carbofuran	chinomethionat (a)	chlordane
chlorfenapyr (i/a)	chlorfluazuron	clofentezine (a)
coumaphos	cryolite	cyfluthrin
beta-cyfluthrin	cyhexatin (a)	cypermethrin
alpha-cypermethrin	beta-cypermethrin	theta-cypermethrin
d2341 (a)	deltamethrin	diafenthiuron (i/a)
dicofol (a)	dienochlor (a)	diflubenzuron
dimethylvinphos	dinobuton (a)	dpx-jw062/dpx-mp062
endosulfan (i/a)	esfenvalerate	etoxazole (a)
fenazaquin (i/a)	fenbutatin oxide (a)	fenpyroximate (a)
fentin (a)	fipronil	flucycloxuron (i/a)
flufenoxuron (i/a)	halofenozide	gamma-hch
heptachlor	hexaflumuron	hexathiazox (a)
hydromethylnon	isoprocarb	lufenuron (i/a)
methiocarb (i/a)	methoxychlor	novaluron
pentachlorophenol	phosmet	pymetrozine
pyridaben	pyridaphenthion (i/a)	pyrimidifen (i/a)
resmethrin	rh-2485	rotenone
spinosad	sulfluramid	szi-121 (a)
tebufenozide	tebufenpyrad (a)	teflubenzuron
tetrachlorvinphos	tetradifon (a)	tetramethrin
thiodicarb	tralomethrin	triflumuron
trimethacarb	xmc	xylylcarb

(I = insecticide A = acaricide (miticide)
PGR = plant growth regulator)

Suitable herbicidal materials having a melting point of at least 55°C and a solubility in water of not more than 600ppm include the following:-

	Herbicides	
ac 94,377 (pgr)	aclonifen	akh-7088
ametryn	amidosulfuron	asulam (<ph4.82)
atrazine	azafenidin	azimsulfuron
bay foe 5043	benazolin	benfluaralin
bensulfuron-methyl	bentazone	benzofenap
bifenox	biphenyl	bromobutide
bromofenoxim	bromoxynil	butralin
butroxydim	butylate	cafenstrole
chlomethoxyfen	chlobomuron	chloridazon
chlorimurorn-ethyl	chlorotoluron	chlorsulfuron
chlorthal-dimethyl	cinosulfuron	clodinaop-propargyl

	Herbicides	
clomeprop	cloransulam-methyl	cyanzine
cyclanilide (pgr)	cyclosulfamuron	2,4-d acid
daimuron	2,4-db	desmedipham
desmetryn	diclobenil	dichlorprop
dichlorprop-p	diclofop-methyl	diflufenican
dimefuron	dimethmetryn	dinitramine
dinoterb	diphenamid	dithiopyr
diuron	ethalfluralin	ethametsulfuron-methyl
ethofumesate	ethoxysulfuron	ethychlozate (pgr)
etobenzanid	fenozaprop-p-ethyl	flamprop-m-isopropyl
flamprop-m-methyl	flumetralin (pgr)	flumetsulam
flumiclorac-pentyl	fluometuron	fluoroglycofen-ethyl
flupoxam	flupyrsulfuron-methyl-sodium	flurenol
fluridone	flurochloridone	fluroxypyr
flurprimidol (pgr)	flurtamone	fluthiacet-methyl
fomesafen	forchlorfenuron (pgr)	halosulfuron-methyl
haloxyfop	imazamox	imazaquin
imazosulfuron	inabenfide (pgr)	indanofan
4-indol-3-ylbutyric acid (pgr)	ioxynil	isoproturon
isouron	isoxaben	isoxaflutole
lenacil	linuron	mcpa
mcpb	mecoprop	mefenacet
mefluidide	metazachlor	methabenzthiazuron
methasulfocarb (pgr)	methyldymron	metobenzuron
metobromuron	metosulam	metsulfuron-methyl
2-(1-naphthyl)acetamide (pgr)	2-(1-naphthyl)acetic acid (pgr)	(2-naphthoxy)acetic acid (pgr)
naproanilide	napropamide	naptalam
neburon	norflurazon	oryzalin
oxadiargyl	oxadiazon	oxasulfuron
oxyfluorfen	paclobutrazol (pgr)	pendimethalin
pentachlorophenol	pentanochlor	pentoxazone
phenmedipham	n-phenylphthlamic acid	picloram
primisulfuron-methyl	prodiamine	prohexadione-calcium (pgr)
prometon	prometryn	propachlor
propanil	propaquizafop	propazine
propham	propyzamide	prosulfuron
pyraflufen-ethyl	pyrazolynate	pyrazosulfuron-ethyl
pyributicarb	pyriminobac-methyl	quinclorac
quinmerac	quizalofop	quizalofop-p
rimsulfuron	sidron	simazine

	Herbicides	
simetryn	sulcotrione	sulfentrazone
sulfometuron-methyl	sulfosulfuron	terbumeton
terbuthylazine	terbutryn	thenylchlor
thiazopyr	thidiazuron (pgr)	thifensulfuron-methyl
tralkoxydim	triasulfuron	tribenuron-methyl
triclopyr	trietazine	trisulfuron-methyl
uniconazole	florasulam	

Particulary suitable fungicides are azoles or triazoles which contain a 1,2,4-triazole group.

In a particularly preferred embodiment, the pesticide is quinoxyfen, cyproconazole, epoxiconazole, florasulam, fenazaquin, oryzalin, isoxaben, glyphosate, (2[2-(3-trifluoromethyl)-5-chloro-2-pyridyloxymethyl)phenyl]-2-methoxyimino-N-methylacetamide, (N-[2-3,5-dimethylphenoxy)-1-methylethyl]-6-(tertiary butyl)-1,3,5-triazine-2,4-diamine or a mixture of two or more thereof.

Particularly preferred mixtures are mixtures of quinoxyfen and cyproconazole, mixtures of quinoxyfen and epoxiconazole, and mixtures of oryzalin, isoxaben and glyphosate.

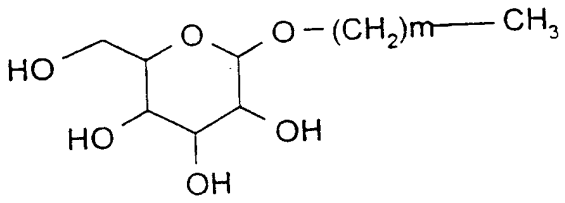
By "adjuvant", is meant a substance which, when added to a formulation of a pesticide, increases its pesticidal efficacy, for example by improving its biological availability.

Whether or not a substance is an adjuvant can easily be determined by one skilled in the art, by using known methods for testing biological efficacy of a pesticide. If the addition of a substance to a pesticidal formulation increases the biological efficacy of the pesticide, then that substance is an adjuvant.

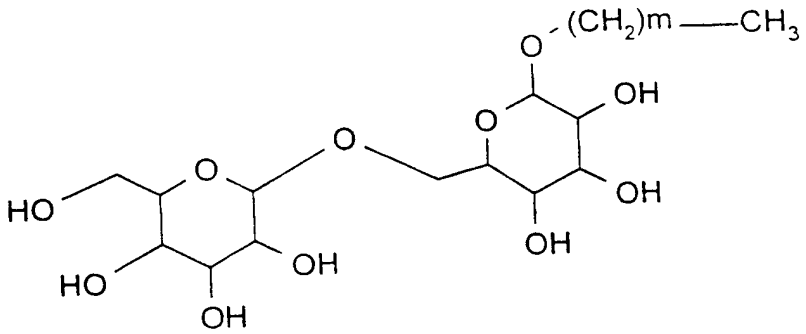
Particularly preferred adjuvants in accordance with the present invention are those known by the following trade names: Atplus 435, Atplus 263, Atplus 264, Atplus 450, Atplus 460, Atplus 469, Atplus 473, Atplus 474, Agrimul PG2067 and Agrimul PG2069, or a mixture of two or more thereof.

Agrimul PG2067 is a mixture of compounds of formula A and B where m is from 7 to 9.

Agrimul PG2069 is a mixture of compounds of formula A and B where m is from 8 to 10.



[A]



[B]

The Atplus surfactants are alkylpolysaccharide blends.

In one embodiment, the adjuvant is present to enhance the biological efficacy of the pesticide which is in particulate form. However, the adjuvant may be present to enhance the activity of a further pesticide in the dispersion, which may not be a particulate suspension. Accordingly, in an alternative embodiment, said formulation additionally comprises a further pesticide, wherein said adjuvant is an adjuvant for said further pesticide. The further pesticide may be dispersed or dissolved in an aqueous or non-aqueous phase, or itself formulated as a particulate suspension.

The amount of adjuvant to be employed is generally from 0.5 to 10 parts by weight based on the total weight of pesticide and

preferably from 1 to 3 parts by weight based the total weight of the pesticide component(s) of the composition.

The amount of the pesticide for which the alkylpolyglycoside is an adjuvant is generally from 25 to 400 g/litre, preferably from 50 to 300 g/litre, based on the whole composition. The amount of additional pesticide present will generally be from 0 to 300 g/litre, preferably from 0 to 200 g/litre.

The amount of adjuvant to be employed based on the total composition is generally from 10 to 600 g/litre, preferably from 200 to 400 g/litre.

Conditions for storage may be any conditions appropriate to the formulation, but will generally be ambient conditions.

The formulation may include any suitable additives known in the art, for example, for example, antifreeze agents, surfactants e.g. anionic and nonionic surfactants, suspension aids (e.g. cellulosic suspension aids or xanthum gum suspensions), antifoams and biocides.

A number of preferred embodiments of the invention are described in the following Examples.

Example 1

A particulate suspension of quinoxyfen and epoxiconazole was prepared as the following millbase:

Millbase	Product g/L
Quinoxyfen	75.0
Epoxiconazole	125.0
Morwet D425 (anionic surfactant blend)	10.0
5% Avicel CL611 (aq) (suspending aid)	40.0
Foamaster UDB (antifoam)	0.8
Water and inerts in a.i.s	149.2
	400.0

Atplus 435 was then added in the following postmill addition:

Postmill Additions	Product g/L
5% Avicel CL611 (aq)	100.0
Atplus 435	375.0
2% Kelzan S (Xanthum gum suspension)+ 1% Proxel GXL (biocide)	50.0
Propylene glycol (antifreeze)	75.0
Proxel GXL	0.5
Water	Balance
	1 litre

Accordingly, the nominal composition was:

	g/L
Quinoxyfen	75.0
Epoxiconazole	125.0
Morwet D425	10.0
Avicel CL611	7.0
Foamaster UDB	0.8
Atplus 435	375.0
Kelzan S	1.0
Proxel glycol	1.0
Propylene glycol	75.0
Water and inerts in a.i.s	Balance
	1 litre

Samples of the formulation were stored in glass at various temperatures for up to 24 weeks. Particle size parameters were measured initially, at 4 weeks and at 24 weeks. The results are shown below in Table I:

TABLE I

Storage Time	Storage Temp (°C)	Particle Size Parameters				
		10%< (µm)	Median (µm)	90%< (µm)	Span	Sp SA (sq.m/g)
Initial	Ambient	0.39	1.73	6.79	3.70	6.5100
4 Weeks						
	-10	0.34	1.78	8.28	4.45	7.0367
Daily cycle	-20/+5	0.35	1.69	8.15	4.61	7.0248
Daily cycle	-5/+30	0.32	1.64	7.58	4.43	7.5011
	Ambient	0.36	1.74	7.98	4.38	6.8367
	40	0.32	1.72	7.96	4.44	7.3592
24 Weeks						
	-10	0.35	1.83	7.87	4.10	6.8840
	Ambient	0.32	1.70	8.72	4.93	7.3639
	30	0.34	1.79	12.26	6.67	6.9693
	40	0.35	2.06	19.10	9.12	6.6016

Sp SA = specific surface area

It was found that no significant crystal growth took place.

Example 2

A particulate suspension of quinoxyfen and epoxiconazole was prepared as in Example 1 with various surfactants employed as adjuvants, namely Atlox 4991, Ethomeen C-25, Pluronic 10500 and Atplus 435. Initial median particle size was 1.24 µm.

Samples of the formulations were stored for two weeks at a -5/30°C daily cycle and at 40°C. The samples were inspected for signs of crystal growth after two weeks, and results are shown in Table II below:

TABLE II

Chemical Class	Trade Name	Supplier	Microscope (x50) after storage (for 2 weeks) at -5/+30°C daily cycle	40°C
Alcohol ethoxylate	Atlox 4991	ICI	40um+ needles	No growth
Amine ethoxylate	Ethomeen C-25	Akzo	40um+	150um
Ethylene oxide/ propylene oxide copolymer	Pluronic 10500	BASF	40-50um needles	hint of growth
Alkylpolyglucoside	Atplus 435	ICI	No change from initial particle size distribution	No growth

The sample prepared with Atplus 435 was the only sample in which there was no crystal growth.

Example 3

Samples of an epoxiconazole 500g/l suspension concentrate were separately tank mixed with Pluronic 10500 and Atplus 435 and were applied to wheat plants (Cv. Galahad) inoculated with Erysiphe graminis infection. The disease level was tested after 10 days treatment, and the results are shown in Table III below:

TABLE III

Epoxiconazole SC+	Disease level (%)
No adjuvant	19
Pluronic 10500	<1.0
Atplus 435	<1.0

It can be seen that the biological efficacy of the formulation which included an adjuvant was significantly better than the formulation with no adjuvant. Furthermore, the alkyl polyglucoside adjuvant was found to be as effective as Pluronic 10500.

Example 4

The effect of various alkyl polyglucoside adjuvants was measured on the biological efficacy of epoxiconazole against Erysiphe graminis. A formulation comprising 500g/l epoxiconazole as a suspension concentrate was tank mixed with adjuvant at a ratio of 1:3 epoxiconazole:adjuvant. The disease level was measured 5 days after treatment. Results are shown in Table IV below:

TABLE IV

Epoxiconazole SC +	Disease level (%)
Atplus 435	3.1
Atplus 263	1.9
Atplus 264	2.9
Atplus 450	3.8
Atplus 460	3
Atplus 469	2.7
Atplus 473	4
Atplus 474	3.85
Agrimul PG2067	9.25
Agrimul PG2069	6.8

In the absence of adjuvant infection levels of 32% were obtained. Untreated plants showed infection levels of 37% five days after treatment.

Example 5

Aqueous dispersion formulations of quinoxyfen, florasulam and fenazaquin were prepared with Atlox 4991 and Atplus 435 as surfactants as shown below:

	%w/w	%w/w
Quinoxyfen 53.5% suspension	12.5	12.5
Atlox 4991	27.0	-
Atplus 435	-	27.0
Water	45.6	45.6
1.5%w/w Kelzan + 0.2%w/w Proxel GXL (aq)	15.0	15.0

	%w/w	%w/w
Florasulam 45% suspension	14.8	14.8
Atlox 4991	27.0	-
Atplus 435	-	27.0
Water	43.2	43.2
1.5%w/w Kelzan + 0.2%w/w Proxel GXL (aq)	15.0	15.0

	%w/w	%w/w
Fenazaquin 43% suspension	15.5	15.5
Atlox 4991	27.0	-
Atplus 435	-	27.0
Water	42.5	42.5
1.5%w/w Kelzan + 0.2%w/w Proxel GXL (aq)	15.0	15.0

The suspension levels were adjusted to give 6.67 %w/w active ingredient in each mixture.

These samples were checked by microscopy after four weeks storage at various conditions. The results are shown in Table V below:

TABLE V

Active ingredient	Surfactant	Microscope Appearance (x50) after 4 Weeks Storage at	
		-5/+30°C daily cycle	40°C
Quinoxyfen	Atlox 4991	Growth up to 40µm	No growth
Quinoxyfen	Atplus 435	No growth	No growth
Florasulam	Atlox 4991	Growth up to 12µm	Growth up to 12µm
Florasulam	Atplus 435	No growth	Trace of growth*
Fenazaquin	Atlox 4991	Growth up to 12µm	Growth up to 12µm
Fenazaquin	Atplus 435	No growth	Some growth up to 12µm - less than with Atlox 4991.

Biological efficacy tests were not carried out. However, the use of Atplus 435 allows the above actives to be formulated with another active which is not readily biologically available without the use of an adjuvant, without promoting significant crystal growth.

Example 6

A formulation of a mixture of oryzalin (240g/l), isoxaben (40g/l) and glyphosate (120g/l) was prepared, with Agrimul PG2067 (100g/l) as an adjuvant for glyphosate (oryzalin and isoxaben do not require an adjuvant). Oryzalin and isoxaben are present as aqueous particulate dispersions (and therefore are vulnerable to crystal growth), and glyphosate is dissolved in the aqueous continuous phase (as its triisopropylamine salt). Particle size analysis was carried out after 24 weeks at various conditions, and the results are shown below in Table VI:

TABLE VI

		Particle size (micron)		
Storage Period	Storage Temperature °C	Median	90%<	10%<
Initial	Ambient	1.31	3.93	0.24
24 Weeks	-10	1.27	4.14	0.20
	30	2.21	6.51	0.22
	40	2.45	7.52	0.21

Example 7

A 10% formulation of (2[2-(3-trifluoromethyl)-5-chloro-2-pyridyloxymethyl)phenyl]-2-methoxyimino-N-methylacetamide (referred to as Compound 3 below) was prepared as an emulsifiable concentrate and its activity against powdery mildew on cereals was compared with the activity of a 10% suspension concentrate of Compound [3]. The suspension concentrate formulation was significantly less active, although its activity was restored by the addition of a wetting adjuvant. It has been found in various screening tests that Pluronic 10500 gives an excellent adjuvant effect, and this was therefore used as a comparator.

Example 8

Field trials were carried out using a one-pack probe suspension concentrate formulation containing 50g/l of Compound 3 and 150g/l Pluronic 10500. This formulation was compared with an emulsion concentrate formulation of compound 3, and with a suspension concentrate containing Atplus 435 as a direct replacement for Pluronic 10500. Compositions are shown in Table VII below.

TABLE VII

(amounts in grams)	SC (no adjuvant)	SC (10500)	SC (Atplus 435)	EC
Compound 3	50	50	50	100
Morwet D425	5	5	5	-
Pluronic 10500	5	5	5	-
Foamaster UDB	1.5	1.5	1.5	-
Propylene glycol	80	-	-	-
Pluronic 10500	-	150	-	-
Atplus 435	-	-	150	-
Kelzan	1.6	1.6	1.6	-
Avicel	9	9	9	-
Water	to 1030	to 1030	to 1030	-
Solvesso 200 (aromatic solvent)	-	-	-	423
N-methyl pyrrolidone (solvent)	-	-	-	423
Tensiofix B7453	-	-	-	54

It was found that all three formulations performed well in the field, but storage at 40°C caused unacceptable crystal growth with the Pluronic 10500 formulations.

Example 9

The formulations prepared in Example 8 were also tested for curative and protective activity against Rust (Puccinia recondita) on winter wheat. The formulations comprising Atplus 435 and Pluronic 10500 gave efficacy similar to the emulsion concentrate formulation.

Example 10

Small sub-samples of the field trial samples prepared for Example 8 were stored in glass vials at 40°C and at -10°C. The samples were evaluated after three months storage using a Malvern Mastersizer to determine the median size, and by visual

characterisation under the microscope. Results are shown in Table VII below:

TABLE VII

	3m at -10°C	3m at 40°C
(i) 50g/l SC (no adjuvant)	1.20µm	1.35µm small angular crystals
(ii) 50g/l SC + Pluronic 10500	1.43µm	16.14µm large rhomboid or lozenge crystals
(iii) 50g/l SC + Atplus 435	1.35µm	1.73µm small angular crystals with a few larger crystals

Example 11

Three formulations of the pesticide of N-[2-3,5-dimethylphenoxy)-1-methylethyl]-6-(tertiary butyl)-1,3,5-triazine-2,4-diamine (referred to below as Compound 6) as suspension concentrates in water were prepared with no added surfactant, 40 parts of Atplus 435 to 1 part Compound 6, and 40 parts of Tensiofix D03 (an alcohol alkoxylate adjuvant) to 1 part Compound 6 respectively.

The formulations had the following composition:

SC concentrate:

Compound 6		52g technical
Morwet D-425		5g
Morwet EFW		1g
Water	to	100g

This was milled to approximately 1.5µm median.

This concentrate was then mixed with adjuvants in following proportions and stored:

Compound 6 concentrate		5g
Adjuvant		20g
Water	to	100g

Samples of the formulations were stored for 1 month at ambient temperature, 40°C and 54°C, and then tested for particle size change. Results are shown in Table IX below:

TABLE IX

Sample Reference	Storage Temperature (°C)	Particle Size (µm)			Microscopy
		Median	90% <	Span	
Initial SC sample		1.50	5.61	3.49	
	Ambient	1.55	4.98	2.96	OK. No significant crystal growth
No added surfactant	40	1.56	5.26	3.13	OK. No significant crystal growth
	54	1.41	4.07	2.60	OK. No significant crystal growth
	Ambient	1.36	3.88	2.58	OK. No significant crystal growth
With Atplus 435	40	1.56	4.16	2.39	OK. No significant crystal growth
	54	1.63	4.60	2.52	OK. No significant crystal growth
	Ambient	1.51	4.30	2.51	OK. No significant crystal growth
with Tensiofix D03 (an alcohol alkoxylate)	40	2.03	5.65	2.48	OK. Larger crystals apparent
	54	3.47	8.94	2.39	Very few agglomerates but larger crystals

Example 12

The formulations prepared in Example 11 were sprayed onto veronica persica (VERPE) veronica hederifolia (VERHE) and viola arvensis (VIOAR) at 0.8 and 3.2 g/ha with x % v/v adjuvant added to the spray tank water (sprayed at 200l/ha). The plants were assessed after 15 days for control of the weeds (expressed as % kill). Results are shown in Table X below:

TABLE X

Compound /adjuvant	Rate of adjuvant	rate a.i per ha	Control of VERHE	Control of VERPE	Control of VIOAR
Atplus 435	0.125%	0.8	13	1	26
	0.25	0.8	10.5	0	19.5
	0.375	0.8	8	6.5	40.5
	0.125	3.2	21.5	6	46.5
	0.25	3.2	13	4	48
	0.375	3.2	14.5	9.8	52
Tensiofix D03	0.125%	0.8	7	0	24.5
	0.25	0.8	10	.5	27
	0.375	0.8	6.5	0	31
	0.125	3.2	16.5	3.5	58.5
	0.25	3.2	16.5	16.5	57
	0.375	3.2	14.5	18.5	53.5

It was found that Atplus 435 had a similar effect on biological efficacy as Tensiofix D03. No significant biological effect was observed in the absence of adjuvant at the rates shown in Table X.

Example 13

Concentrates (suspensions in water) of cyproconazole and quinoxyfen were prepared separately as set out in (a) and (b) below via a wet milling (bead milling) process. These were then blended with the adjuvant (Atplus 435) and other components as set out in (c) below.

(a) Cyproconazole concentrate

	%w/w
Water	33.6
5%w/w Avicel CL611 gel (+ 0.1% Proxel GXL)	10.0
Morwet D425	5.9
10%w/w Foamaster UDB	0.5
Propylene Glycol	5.0
Cyproconazole technical	45.0

(b) Quinoxyfen concentrate

Ingredient	%w/w
Quinoxyfen	53.50
Propylene Glycol	5.30
Avicel CL611	0.53
Foamaster UDB	0.13
Kelzan S	0.08
Proxel GXL	0.12
Morwet D425	2.12
Water plus inerts in Quinoxyfen technical	38.22

(c) Concentration: 75g/l Quinoxyfen + 80g/l Cyproconazole

Final composition	%w/w
Water	24.04
Propylene glycol	5.50
1.5%w/w Kelzan S gel (+ 0.2% Proxel GXL)	8.00
5%w/w Avicel CL-611 gel (+ 0.1% Proxel GXL)	10.00
Atplus 435	22.10
Foamaster UDB	1.00
53.5%w/w Quinoxyfen manufacturer's concentrate	12.96
45%w/w Cyproconazole post mill	16.40

Samples of the formulation were stored at various storage temperatures, and particle size parameters were measured, after two and 16 weeks storage. Results are shown below in Table XI:

Table XI

Storage Time (weeks)	Storage Temp (°C)	Particle size parameters			
		d(v, 0.5) (µm)	d(v, 0.1) µm	d(v, 0.9) µm	Span
Initial	Ambient	2.41	0.31	11.95	4.82
2					
daily cycle	-10	1.59	0.28	6.39	3.85
	-5/30	2.10	0.30	8.23	3.78
daily cycle	-20/5	2.02	0.30	7.93	3.78
16					
	-10	2.04	0.29	8.9	4.22
	30	1.84	0.28	8.46	4.45
	40	1.98	0.29	8.61	4.20

Example 14

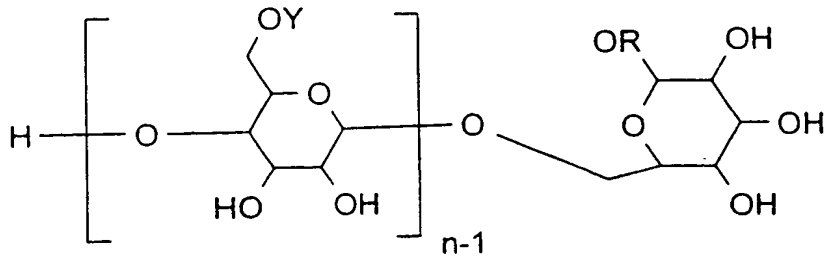
Formulations of cyproconazole (200g/l) were prepared as suspension concentrates in water, with and without Atplus 435 as an adjuvant. The biological activity of the formulations was tested against Erysiphe graminis tritici infection, and results are shown in Table XII below:

	% infection
Cyproconazole SC alone	19.85
1:1 Cyproconazole SC + Atplus 435	0.90
1:3 Cyproconazole SC + Atplus 435	0.55
Untreated plants	20.00

It should be noted that biological activity of a suspension concentrate of quinoxyfen is not significantly increased by the addition of an adjuvant. Accordingly, the effect on the biological activity of cyproconazole only was tested.

CLAIMS

1. The use of an alkyl polyglycoside of general formula [1]



[1]

in a formulation comprising a particulate aqueous suspension of at least one pesticide, as a non-crystal-growth-promoting pesticidal adjuvant,

wherein

R is a C_4-C_{20} alkyl group

n is from 1 to 10,

and Y is H, C_1-C_{20} alkyl, or a group of the formula $(C_qH_{2q}O)_zX$, $-SO_3M$, $-PO_3X_2$, $-COCH_2CH[SO_3M]COOX$, $-COX$, $-(CH_2)_pCOOX$, $-CH_2CH_2SO_3M$, $-COOX$, a quaternary ammonium derivative, or a glycerol residue,

wherein z is from 1 to 50

p is from 1 to 20

q is from 2 to 4

M is H or a suitable counter-ion,

and each X independently is H or C_1-C_{20} alkyl.

2. The use as claimed in claim 1, wherein the pesticide has a solubility in water of not more than 600ppm.

3. The use as claimed in claim 2, wherein the pesticide has a solubility in water of not more than 150ppm.

4. The use as claimed in claim 3, wherein the pesticide has a solubility in water of not more than 50ppm.

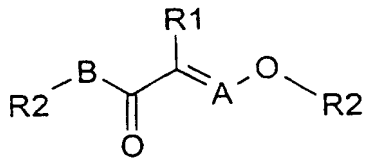
5. The use as claimed in any one of the preceding claims, wherein the pesticide has a melting point of at least 55°C.

6. The use as claimed in any one of the preceding claims, wherein the pesticide has a melting point of at least 77°C.

7. The use as claimed in any one of the preceding claims, wherein the pesticide has a melting point of at least 100°C.

8. The use as claimed in Claim 1, wherein the pesticide contains a 1,2,4-triazole group.

9. The use as claimed in any one of the preceding claims, wherein the pesticide is a compound of the formula [2]:



[2]

wherein R1 is an aromatic or heteraromatic group,
R2 is H, or C_1-C_{10} alkyl
A is CH or N and
B is O or NH.

10. The use as claimed in Claim 9, wherein R1 is phenyl or substituted phenyl.

11. The use as claimed in Claim 9, wherein the pesticide is (2[2-(3-trifluoromethyl)-5-chloro-2-pyridyloxymethyl)phenyl]-2-methoxyimino-N-methylacetamide, kresoxim methyl, or azoxystrobin.

12. The use as claimed in Claim 1, wherein the pesticide is quinoxyfen, cyproconazole, epoxiconazole, florasulam, fenazaquin, oryzalin, isoxaben, glyphosate, (2[2-(3-trifluoromethyl)-5-chloro-2-pyridyloxymethyl)phenyl]-2-

methoxyimino-N-methylacetamide, N-[2-3,5-dimethylphenoxy)-1-methylethyl]-6-(tertiary butyl)-1,3,5-triazine-2,4-diamine, or a mixture of two or more thereof.

13. The use as claimed in Claim 12, wherein the pesticide is a mixture of quinoxyfen and epoxiconazole, a mixture of quinoxyfen and cyproconazole, or a mixture of oryzalin, isoxaben and glyphosate.

14. The use as claimed in any one of the preceding claims, wherein said formulation additionally comprises a further pesticide, wherein said adjuvant is an adjuvant for said further pesticide.

15. The use as claimed in any one of the preceding claims, wherein n is from 1 to 3.

16. The use as claimed in any one of the preceding claims, wherein R is a C_8-C_{18} alkyl group.

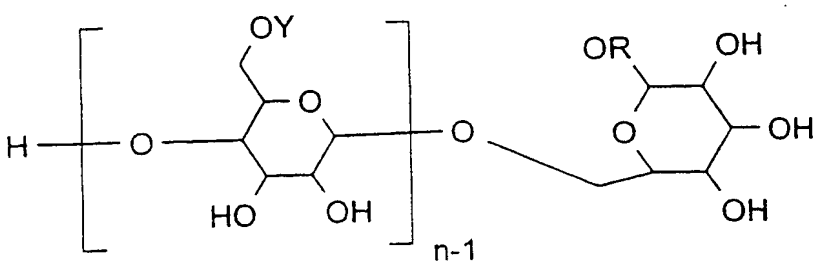
17. The use as claimed in any one of the preceding claims, wherein Y is H.

18. The use as claimed in any one of the preceding claims, wherein the alkyl polyglucoside is Atplus 435, Atplus 263, Atplus 264, Atplus 450, Atplus 460, Atplus 469, Atplus 473, Atplus 474, Agrimul PG2067 and Agrimul PG2069, or a mixture of two or more thereof.

19. The use as claimed in any one of the preceding claims, wherein the amount of said adjuvant is from 0.5 to 10 parts by weight per part by weight of the total pesticide in the composition.

20. The use as claimed in Claim 19, wherein the amount of said adjuvant is from 1 to 3 parts by weight per part by weight of the total pesticide in the composition.

21. The use of an alkyl polyglycoside of general formula [1]



[1]

as a non-crystal-growth-promoting pesticidal adjuvant in an aqueous particulate suspension pesticide formulation, comprising quinoxyfen; epoxiconazole; florasulam; fenazaquin; oryzalin, isoxaben glyphosate; (2[2-(3-trifluoromethyl)-5-chloro-2-pyridyloxymethyl)phenyl]-2-methoxyimino-N-methylacetamide; (N-[2-3,5-dimethylphenoxy)-1-methylethyl]-6-(tertiary butyl)-1,3,5-triazine-2,4-diamine, or a mixture of two or more thereof:-

wherein

R is a C_4-C_{20} alkyl group

n is from 1 to 10,

and Y is H, C_1-C_{20} alkyl, or a group of the formula $(C_qH_{2q}O)_zX$, $-SO_3M$, $-PO_3X_2$, $-COCH_2CH[SO_3M]COOX$, $-COX$, $-(CH_2)_pCOOX$, $-CH_2CH_2SO_3M$, $-COOX$, a quaternary ammonium derivative, or a glycerol residue,

wherein z is from 1 to 50

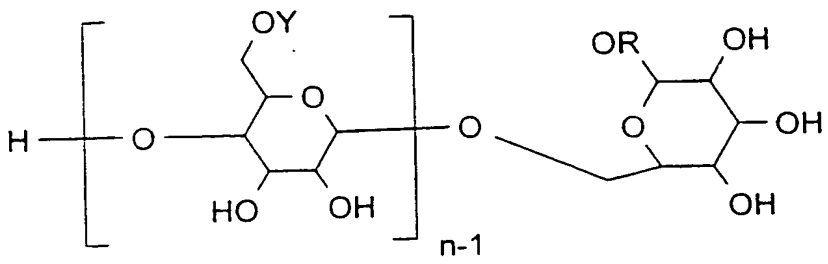
p is from 1 to 20

q is from 2 to 4

M is H or a suitable counter-ion,

and each X independently is H or C_1-C_{20} alkyl.

22. The use of an alkyl polyglycoside of general formula [1]



[1]

as a non-crystal-growth-promoting fungicidal adjuvant, in an aqueous particulate suspension formulation comprising quinoxyfen and cyproconazole,

wherein

R is a C_4-C_{20} alkyl group

n is from 1 to 10,

and Y is H, C_1-C_{20} alkyl, or a group of the formula $(C_qH_{2q}O)_zX$, $-SO_3M$, $-PO_3X_2$, $-COCH_2CH[SO_3M]COOX$, $-COX$, $-(CH_2)_pCOOX$, $-CH_2CH_2SO_3M$, $-COOX$, a quaternary ammonium derivative, or a glycerol residue,

wherein z is from 1 to 50

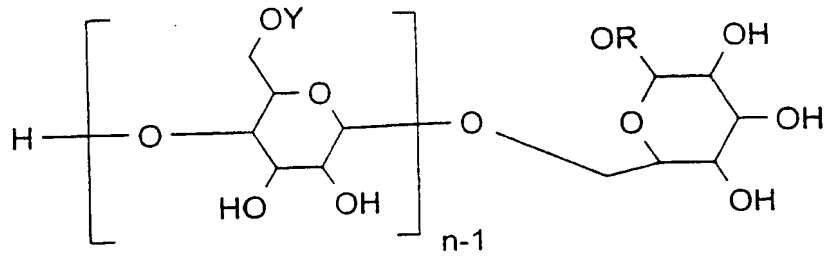
p is from 1 to 20

q is from 2 to 4

M is H or a suitable counter-ion,

and each X independently is H or C_1-C_{20} alkyl.

23. The use of an alkyl polyglycoside of general formula [1]



[1]

in a formulation comprising a particulate aqueous suspension of at least one pesticide, as a non-crystal-growth-promoting pesticidal adjuvant,

wherein

R is a C_4-C_{20} alkyl group

n is from 1 to 10,

and Y is H, C_1-C_{20} alkyl, or a group of the formula $(C_qH_{2q}O)_zX$, $-SO_3M$, $-PO_3X_2$, $-COCH_2CH[SO_3M]COOX$, $-COX$, $-(CH_2)_pCOOX$, $-CH_2CH_2SO_3M$, $-COOX$, a quaternary ammonium derivative, or a glycerol residue,

wherein z is from 1 to 50

p is from 1 to 20

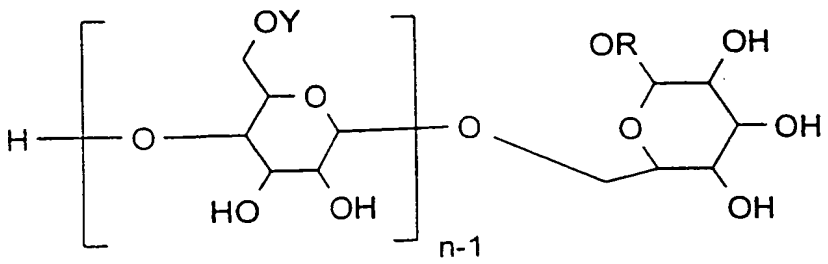
q is from 2 to 4

M is H or a suitable counter-ion,

and each X independently is H or C_1-C_{20} alkyl

but wherein said pesticide is not a mixture of quinoxyfen and cyproconazole.

24. A method of increasing the biological efficacy of a pesticidal active composition comprising a particulate aqueous suspension of at least one pesticide, whilst preventing unacceptable crystal growth in the composition, which method comprises incorporating in the composition an alkyl polyglycoside of general formula [1]



[1]

as a non-crystal-growth-promoting pesticidal adjuvant,

wherein

R is a C_4-C_{20} alkyl group

n is from 1 to 10,

and Y is H, C_1-C_{20} alkyl, or a group of the formula $(C_qH_{2q}O)_z X$, $-SO_3M$, $-PO_3X_2$, $-COCH_2CH[SO_3M]COOX$, $-COX$, $-(CH_2)_pCOOX$, $-CH_2CH_2SO_3M$, $-COOX$, a quaternary ammonium derivative, or a glycerol residue,

wherein z is from 1 to 50

p is from 1 to 20

q is from 2 to 4

M is H or a suitable counter-ion,

and each X independently is H or C_1-C_{20} alkyl.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/GB 99/00837

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N25/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 42 29 442 A (HENKEL KGAA) 10 March 1994 cited in the application see page 2, line 51 - line 54 see page 4, line 15 - line 19 ---	1-24
X	DE 35 45 908 A (HENKEL KGAA) 25 June 1987 cited in the application see claims 1,9 see page 3, line 54 - line 59 ---	1-24
X	US H224 H (A.H. MALIK ET AL.) 3 March 1987 cited in the application see column 2 --- -/--	1-24

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search	Date of mailing of the international search report
18 June 1999	25/06/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Decorte, D

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ENSDOCID: <WO 9948359A1 | >

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/GB 99/00837

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 22917 A (HENKEL CORP) 25 November 1993 cited in the application see page 6, line 3 - line 7 see page 7, line 4 - line 9 see page 34, line 18 - line 20	1-24
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